

PEOPLE
MARIE CURIE ACTIONS

Intra-European Fellowships (IEF)

Call: FP7-PEOPLE-2013-IEF

“Main group element catalysts and bond activation reagents”

“MGpCat”

“Main group element catalysts and bond activation reagents”

Evgeny L Kolychev and Simon Aldridge - University of Oxford

1. Executive Summary:

The Marie Curie project ‘Main group element catalysts and bond activation reagents’ was at the original schedule by mutual agreement between the fellow (Dr Evgeny L Kolychev) and the host (Prof Simon Aldridge), and was undertaken in the Chemistry Research Laboratory, Department of Chemistry, University of Oxford between June 2014 and May 2016. The training acquired by the fellow both in technical/scientific aspects of the project and in more general management, organizational, communication and planning aspects are very important for Dr Kolychev’s scientific career.

Dr Kolychev’s work during his time in Oxford has given rise to four publications to date, including papers in the top-ranking chemistry journals *Journal of the American Chemical Society* (three) and *Chemistry – European Journal* (one). One further paper is under consideration currently (with *Journal of the American Chemical Society*) and three-four more will be submitted in the coming six-month period. In addition, Dr Kolychev was afforded the opportunity to present his work at a number of national and international meetings, including conferences organized by the Royal Society of Chemistry (*2016 RSC Coordination and Organometallic Chemistry Discussion Group Meeting*, presented poster), *IMEBORON 2014* meeting and the *14th International Symposium on Inorganic Ring Systems (IRIS)* in Regensburg, Germany (July 2015; presented poster). In addition Dr Kolychev was one of the founder organizing members of the Oxford Chemistry Department’s postdoctoral seminar programme, which has run for the past 12 months. This scheme – which is entirely run by research fellows and post-doctoral associates, invites external speakers in Organometallic and Main Group chemistry, organizes their programme on the day(s) of the visit and is responsible for all logistical aspects of the visits.

Scientifically Dr Kolychev’s output from the project has been prodigious, including the synthesis of novel organic ligands which can be used for the design of diboryl compounds and establishing fundamental bases for creation of chelate diboryl anionic ligands. This work – while fundamental in its nature offers enormous potential going forward in the developing area of main group element coordination compounds with transition metal reactivity in stoichiometric as well as in catalytic conditions. Catalysis is central to wealth creation in modern chemicals/materials manufacture, and the use of new, environmentally friendly and cost-effective catalysts based on main group elements offers a potentially transformative alternative to the continuing use of expensive and toxic heavy transition metal systems.

From a technical perspective, we targeted a number of ligand frameworks for the formation of multi-dentate poly-anionic boryl ligand systems. In particular we targeted Main group element complexes of these ligands as a mechanism for controlling complex geometry and through this approach tune the redox properties of the Main group metal centre. Using this approach redox-based bond modification using these non-typical metals can be targeted – and indeed this is one of the key findings in a recently accepted paper in *J. Am. Chem. Soc.* to which Dr Kolychev contributed a large amount (*J. Am. Chem. Soc.*, **2016**, 138, 4555-4564).

In addition, Dr Kolychev's work has developed novel procedures for the efficient synthesis of novel dianionic tetra- and penta-dentate ligands which could then be used to prepare bis-boronbromido or boronhydrido species. The use of these species in the formation of related metal complexes is an area of research which is being continued going forward in the host group. Transformation of the bidentate and tridentate ligands to corresponding stannylene complexes and their stoichiometric reactivity to viable catalytic processes has not yet been achieved, but represents one of the major goals of the project going forward, and one which will be enabled by the significant ground work established by Dr Kolychev during the period of the Fellowship.

Additionally a novel and more convenient procedure for the preparation of boryl zinc compounds in one step starting from the boronbromide has been developed. This is potentially ground-breaking, given the difficulty in preparing boryl-metal species directly, and the fact that borylzinc complexes can be utilized directly in a novel bora-Negishi C-B bond forming methodology (manuscript currently under consideration by *J. Am. Chem. Soc.*).

2. Summary description of project context and objectives:

Catalysis is critical to the delivery of future growth in the manufacturing sector: ca. 75% of all chemicals currently require catalysts at some stage in their manufacture, with catalytic processes generating €800 bn in products worldwide. In the US, for example, catalysis and catalytic processes account for ca. 20% of GDP, with 30 of the 50 largest volume chemicals currently produced via catalytic routes. The development and fundamental understanding of innovative new catalyst systems therefore has clear, direct and long-term benefits to the chemical manufacturing sector and to the broader knowledge-based economy.

The selectivity, tune-ability and amenability to mechanistic investigation of homogenous catalysts mean that such systems are widely employed in key industrial processes allied to pharmaceutical, polymer, and bulk chemical manufacture. This proposal targets a step-change in homogenous catalysis by approaching it from an entirely new perspective. The vast majority of current industrial catalysts use expensive late Transition Metals (e.g. Rh, Pd, Pt); increasing scarcity, exacerbated by global industrialization, has led to a sharp increase in the cost of such commodities. Current prices of Rh (US\$ 65,000/kg) and Pt (US\$ 55,000/kg), for example, mean that precious metal recovery is now a major growth sector. By contrast, catalysts utilizing inexpensive/abundant *s* and *p*-block elements have recently begun to emerge. Drawing on this theme, this proposal aiming for utilizing elements costing a fraction (ca. 2-3%) of widely used precious metals, and seeks to develop viable processes based on single-site/binuclear (single-component) Main Group catalysts. In recent years, research into Main Group compounds has highlighted the accessibility of low-valent derivatives with vacant coordination sites, and frontier orbitals with relatively small HOMO-LUMO energy gaps able to facilitate bond activation by oxidative addition. Thus, a mode of reactivity typical of late Transition Metals has been opened up; complementary strategies utilizing constant oxidation state processes (e.g. σ -bond metathesis) have also emerged. Thus, the opportunity to exploit Main Group elements, once perceived as catalytically inert, as novel catalysts is not only at the cutting edge scientifically, but also offers huge potential for growth.

With regard to redox-based processes, Main Group systems capable of effecting oxidative activation of E-H bonds are now known (for E = H, C, N, O, Si). However, reagents capable of such insertion chemistry are typically highly reactive species, which suffer from a lack of selectivity. Perhaps more critically, the use of sub-valent Main Group compounds in E-H bond activation processes typically generates products in thermodynamically very stable oxidation states. Catalytic turnover via reductive regeneration of the active species similar to late Transition Metal catalysis is thus difficult to effect. However, recent work from the Aldridge group and that of Radosevich, gives encouragement that catalytic cycles based on $n/n+2$ oxidation

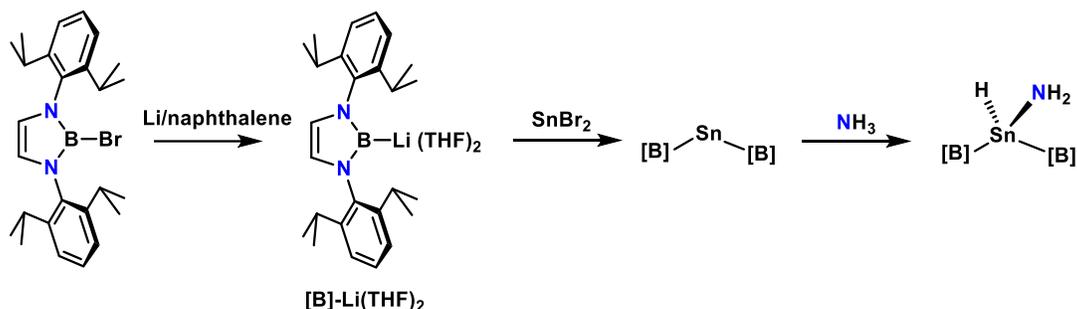
states for *Main Group elements* are indeed viable. The overall aim of the work is to explore the viability and scope of Main Group (mainly ecologically benign Ge systems) based catalysis. We stress that the aim at this stage is not necessarily to identify immediate replacements for existing Transition Metal systems in societally important catalytic transformations, but rather to establish the fundamental ground rules for catalyst design in what is an entirely new area of endeavor.

The chemistry of multiply bonded species featuring the heavier Group 14 elements silicon-lead has attracted significant attention in recent years, reflecting fundamental differences in electronic/ geometric structure from their carbon congeners and their associated potential for exploitation in bond activation, and ultimately in catalysis. The synthesis in the early 1980s of landmark compounds featuring Si=C and Si=Si bonds, initiated investigation across a broad field spanning catalytic and materials science. One of the intrinsic challenges associated with the isolation of systems containing M=E double bonds (where E = C, N, O, for example) is the thermodynamic incentive for aggregation presented by the formation of strong M-E single (sigma) bonds. A highly successful approach to circumvent this problem makes use of extremely bulky peripheral substituents and the increase in coordination number implicit in aggregation. Alternative strategy - which to our knowledge has been explored only in transition metal functionalized systems - involves the use of a net cationic charge at the Group 14 center to provide an electrostatic disincentive to oligomerization. Additional stabilization of the Main Group centre via the chelate effect could be achieved by using bidentate diboryl ligands. A proposed exemplar synthesis of these ligands consists of the condensation of a diamine with an iminoacetaldehyde followed by borylation, bromination and reduction. Studies have shown that the boryl ligand of the type [B(NR'₂)₂] as an extremely strongly σ -donating class of ligand. As such, its incorporation as one (or both) of the R substituents at a singlet tetrelene R₂E: (such as a silylene or carbene) would be expected to raise significantly the energy of the HOMO. Thus, if sufficient steric bulk can be incorporated to prevent dimerization, boryl substituents can be perceived as 'bespoke' ancillary substituents for the generation of singlet tetrelene {(R'₂N)₂B}R₂E: possessing a reduced HOMO-LUMO gap. As others have noted, reduction of this gap is critical for E-H bond activation, ultimately in catalysis, since it implies easier access to the required triplet excited state.

3. Description of the main S&T results and foreground:

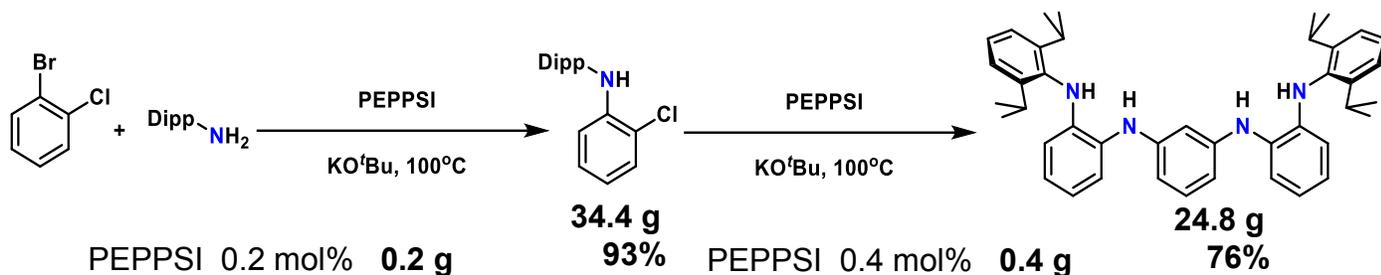
At the start of the project we together with Dr. Andrey Protchenko studied activity of the diboryl stannylene and found out that the compound can activate ammonia at very mild conditions (Scheme 2). The results are summarised in a paper and submitted to the Journal of American Chemical Society.

Scheme 2

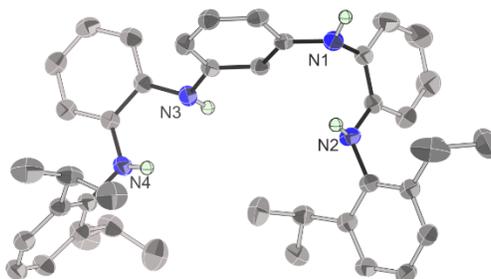


After that study we are focused on design of chelate diboryl ligands. At first we started from a known from literature sources tetraaniline (Scheme 3). We optimised the synthetic procedure for the preparation of this compound applying N-heterocyclic carbene based catalyst – PEPPSI. The novel procedure allowed to obtain the tetraaniline in a high yield at a multi-gram scale synthesis. Moreover, the structure of the compound were established by X-ray diffraction (Picture 1).

Scheme 3



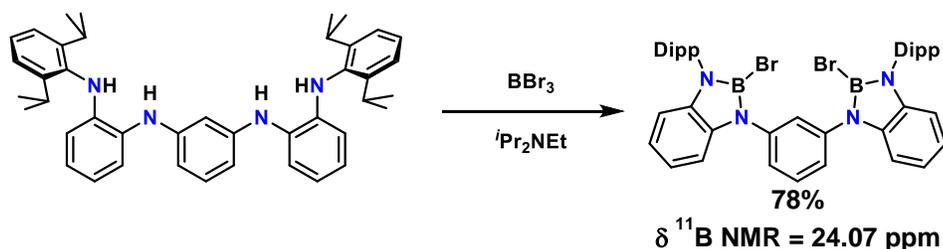
Picture 1



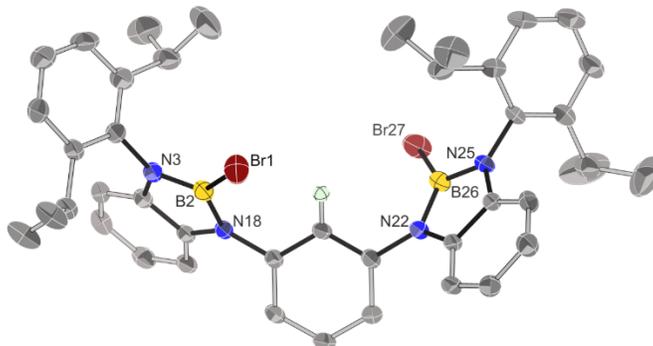
The compound further reacted with tribromoborane to produce bis(bromoborane). This compound

was fully characterised and the structure of it was established by X-ray crystallography (Scheme 4, Picture 2). The key structural parameters of the compound are B-Br = 1.898 Å, N-B-N = 108.4°. At the next step we studied the properties of this novel bis(bromoborane). Thus, it reacts with small nucleophiles such as ammonia to produce a bis(aminoborane). Additionally, the compound could be reduced to form a bis(hydroborane) - a valuable precursor for the synthesis of diboryl complexes by an oxidative addition. Furthermore, both the bis(bromoborane) and bis(hydroborane) react with moisture from air to form bis(hydroxyborane) (Scheme 5, Picture 3). All the products were fully characterised and the important parameters of the structures are: B-O: 1.349-1.351 Å, O...H: 2.8-2.9 Å; N-B-N: 106.80-105.92°; B-N: 1.391-1.398 Å, N-B-N: 105.77-105.81°.

Scheme 4

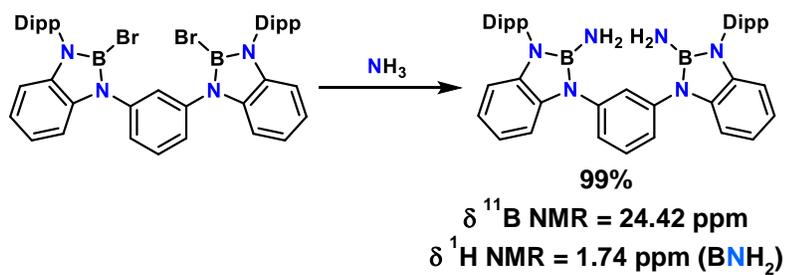
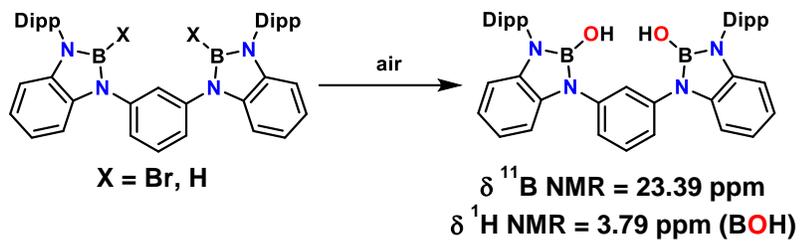
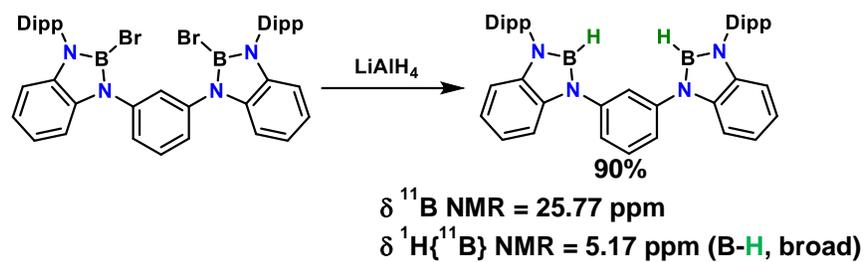


Picture 2

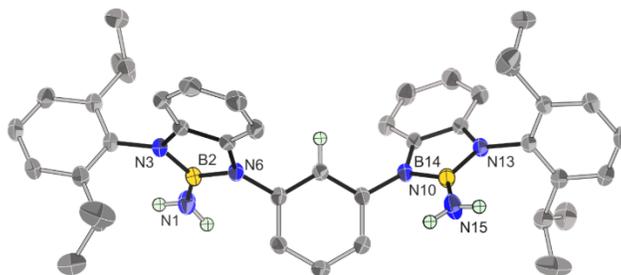


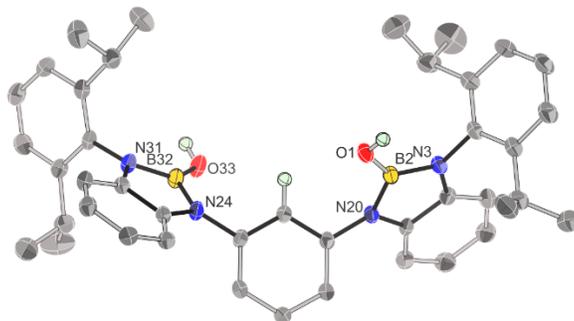
Bis(bromoborane) was further modified to simplify its reactivity with nucleophiles by reaction with pyridine. The reaction gives a bis(borenium) cation which will react easily with any nucleophilic metal source such as $\text{Na}_2\text{Fe}(\text{CO})_4$ forming bis(boryl) complexes (Scheme 6). The compound was structurally characterised and the X-ray study confirmed its bis(cationic) nature (see Picture 4).

Scheme 5

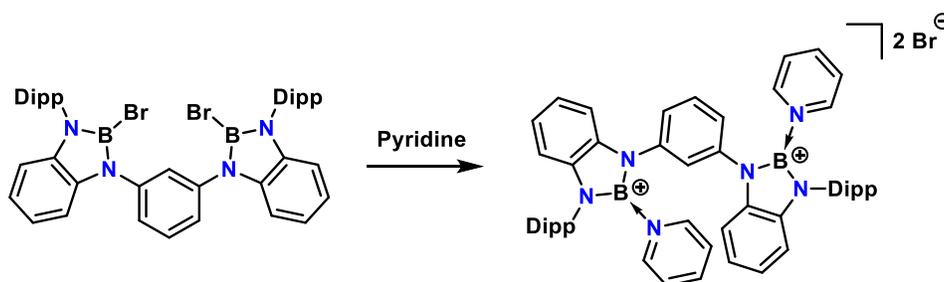


Picture 3

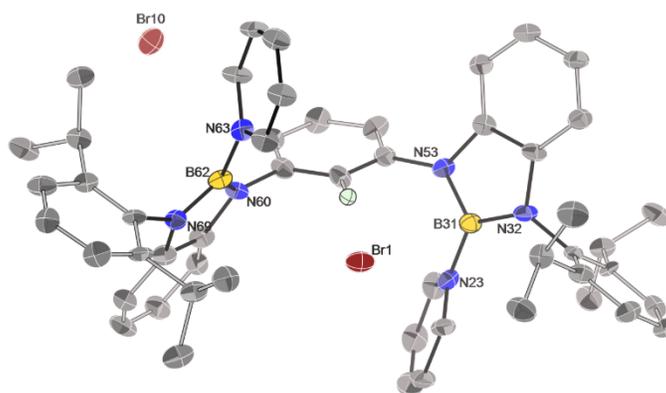




Scheme 6



Picture 4



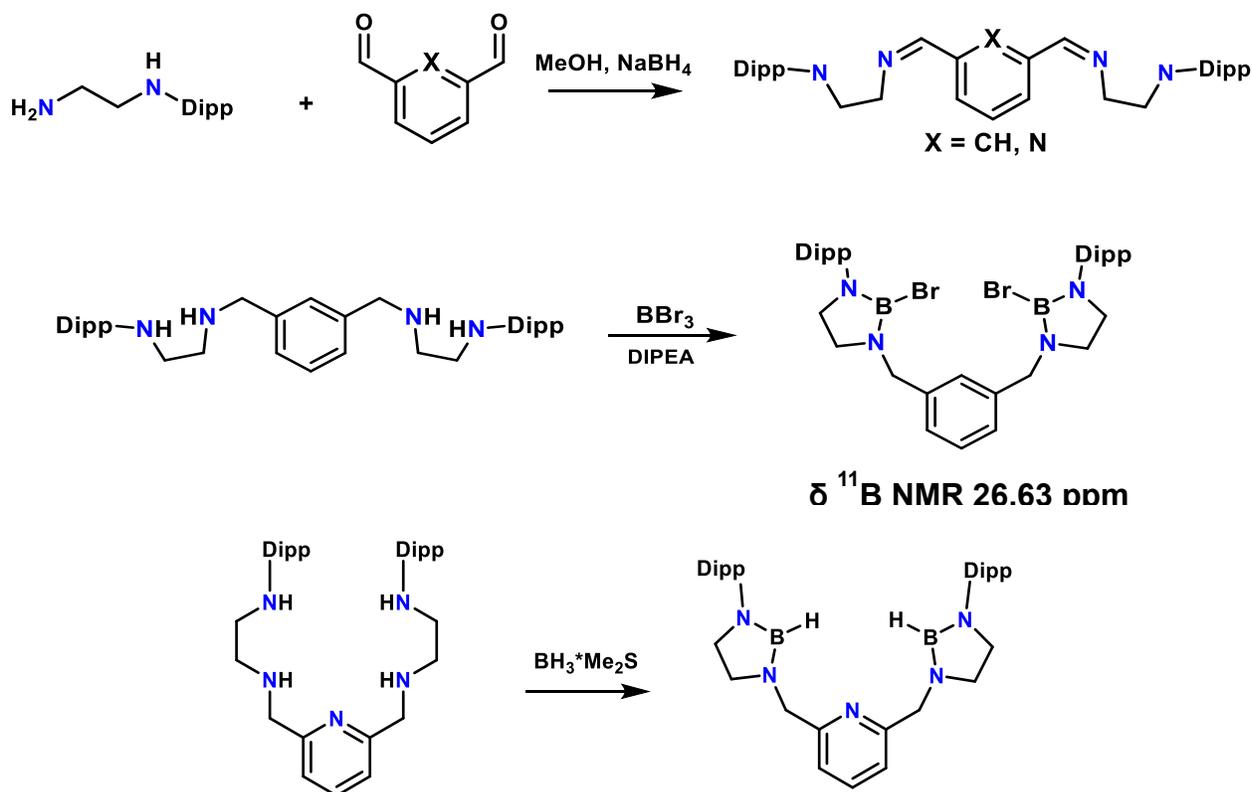
At the next step of the research investigation we looked into possibilities to modify the structure of bis(boryl) ligands. The two main parameters studied are: 1) addition of a rigid CH_2 bridge to control the bite angle of a dianionic ligand; 2) addition of a neutral donor such as pyridyl bridge; 3) development of the a trianionic B-C-B system. CH_2 bridged compounds were accessible via straightforward reductive amination route (Scheme 7). In this case both the phenyl and the pyridyl bridged tetraanilines were synthesised by the similar synthetic procedure. However, it was possible to synthesise the bis(bromoborane) only for the phenyl bridged system, whereas the pyridyl bridged tetraaniline react with tribromoborane with formation of a complex mixture of products. In the last case bis(hydroborane) was prepared as an alternative ligand source.

Also, the saturated versions of the bis(boryl) ligands were accessed by two different synthetic routes: 1) a phenyl bridged tetraamine was prepared by a consecutive acylation, alkylation and reduction; 2) the

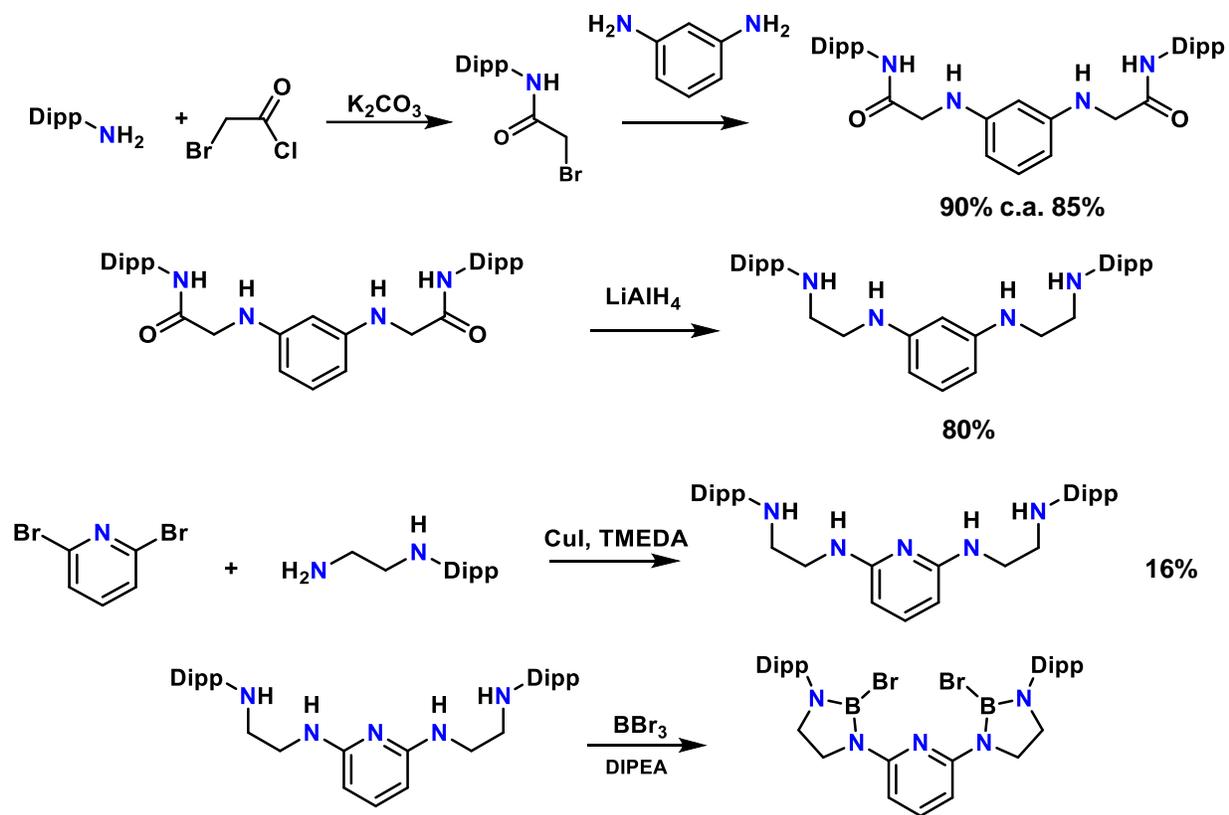
pyridyl bridged system can be prepared by a more straightforward copper catalysed C-N cross-coupling of diisopropylphenyl ethylenediamine and dibromopyridine (Scheme 8). It is worth to mention, that an unsaturated pyridyl bridged ligand was also prepared by cross-coupling of chloronitrobenzene with diisopropylaniline followed by a reduction and a second cross-coupling with dibromopyridine (Scheme 9). During this synthesis the intermediate pyridyl tetraaniline as well as the final bis(bromoborane) were isolated and fully characterised including single crystal X-ray diffraction (Picture 5).

To sum up, at the moment we have developed the reliable synthetic routes to a range of the precursors for bis(boryl) metal complexes. At the next step of the project we will attempt to prepare bis(boryl) complexes of Main Group elements either by reduction of the bis(bromoboranes) followed by a metathesis reaction with MX_2 sources or a oxidative addition to the bis(hydroboranes).

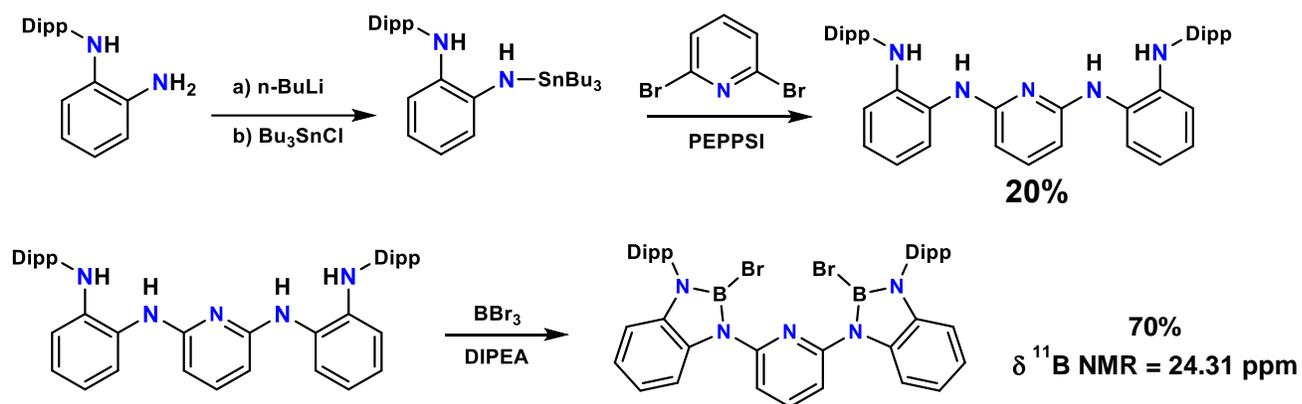
Scheme 7



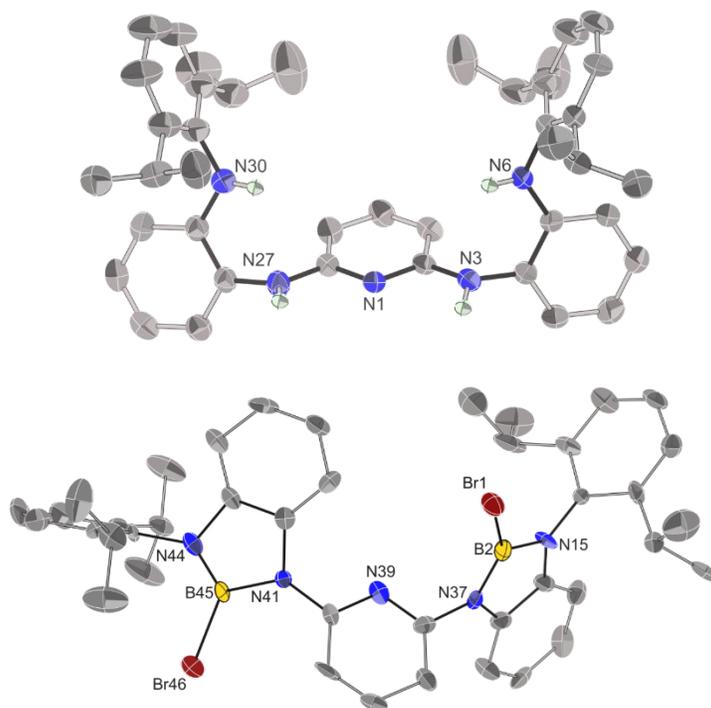
Scheme 8



Scheme 9



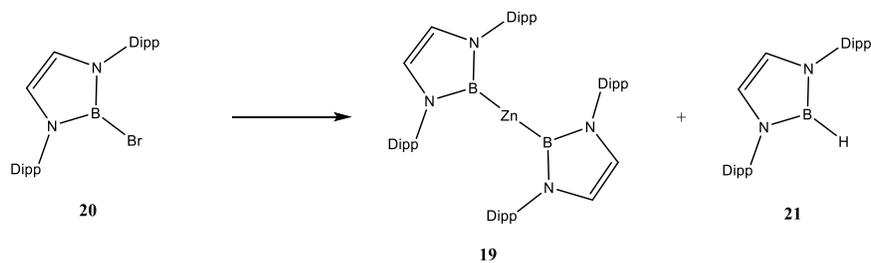
Picture 5



Additionally, since synthesis of borylzinc reagents via current literature procedures involves transmetalation from the boryllithium complex $(\text{thf})_2\text{Li}\{\text{B}(\text{NDippCH})_2\}$, the synthesis of which involves maintaining the reaction mixture for 2 days at -45°C , and is very sensitive to the reaction conditions and the purities of the reagents/solvents involved. We therefore made attempts to find alternative routes to the borylzinc reagents central to this study. Recently, Yamashita and co-workers reported preliminary results showing that boryllithium species can be generated in hydrocarbon solvents using a complex mixture of metallic lithium, sodium and potassium together with a large excess of lithium chloride. Our investigations, on the other hand, show that pure lithium or sodium sands in isolation do not reduce bromoborane, while the reaction with potassium sand gives solely the hydroborane, consistent with reduction by potassium, but with unworkable lability for the K-B bond. With this in mind, we next performed the potassium reduction in the presence of various zinc salts with the aim of effecting in situ transfer of the boryl fragment to zinc. Reactions with zinc(II) acetate, zinc(II) triflate or diethylzinc result in the formation of complex mixtures of products, but reduction in the presence of either zinc(II) chloride or bromide gives binary mixtures of

hydroborane and diborylzinc in yields of ca. 60% and 40%, respectively (see Table 1). Diboryl zinc is inactive in the bora-Negishi coupling reaction, however it can easily be transformed into the active boryl zinc reagent in situ by addition of ZnBr_2 .^b Further optimization of the direct synthesis of diboryl zinc was attempted by the addition of excess lithium chloride, which did not change the ratio of products. Attempts carry out the reduction at lower temperatures resulted in lower conversions to the same mixture of products, and reactions in benzene or toluene resulted in selective reduction of zinc dihalides to metallic zinc. Thus, the optimal reduction conditions in our hands were found to involve 4.4 equiv. of potassium sand, 2 equiv. of ZnCl_2 and *n*-hexane as the solvent. Finally, we were able to scale up the reaction to 1 g scale and isolate pure diborylzinc in 31% yield, an outcome which is comparable to that reported for the synthesis via a boryllithium intermediate,^b but with the additional convenience of a single step and without the need of maintaining low temperatures for long periods of time.

Table 1. Attempted reductions of the boryl bromide^a



Entry	Reductant	Solvent	Zn source	$[\text{B}]_2\text{Zn}$, % ^b	$[\text{B}]\text{H}$, % ^b	$[\text{B}]\text{Br}$, % ^b
1	Li	<i>n</i> -hexane	-	0	0	100
2	Na	<i>n</i> -hexane	-	0	0	100
3	K	<i>n</i> -hexane	-	0	100	0
4	K	<i>n</i> -hexane	ZnCl_2	42	58	0
5	K	<i>n</i> -hexane	ZnBr_2	40	60	0
6	K	<i>n</i> -hexane	$\text{Zn}(\text{OAc})_2$	0	0	0
7	K	<i>n</i> -hexane	$\text{Zn}(\text{OTf})_2$	0	0	0
8	K/LiCl	<i>n</i> -hexane	ZnCl_2	40	60	0

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11	K	<i>n</i> -hexane	ZnCl ₂	11	18	71
9	K	toluene	ZnCl ₂	0	0	100
10	K	benzene	ZnCl ₂	0	0	100

a: reaction conditions, 0.5 mmol of boryl bromide, 4.4 eq. of alkali metal sand, 2 eq. of Zn salt, 5 mL of solvent, vigorous stirring for 24 hours. b: spectroscopic yields according to ¹H and ¹¹B NMR.

4. Potential impact and the main dissemination activities and exploitation of results:

Before coming to Oxford with Marie-Curie fellowship, I have proved my ability to contribute to a challenging synthetic programme in one particular area of organometallic chemistry. I have also shown myself to be adaptable to new ways of working and extremely competent in the acquisition of new techniques. My research profile and the results I secured during both my PhD and postdoctoral studies, together with my publication record reflect my unique ability to acquire new competencies promptly and to apply them to solve the synthetic problems faced on a daily basis. However, the primary focus of the proposed Fellowship project was chemically distinct from my previous 'comfort zone' and involved broadening my expertise into a more diverse range of chemical systems, notably within the Main Group system. In terms of future career options and marketability, and ability to apply my skills across a broader spectrum of societal challenges, this chemical diversification is a key driving benefit of the Fellowship.

In addition, the proposed Fellowship brought with it a number of additional non project-specific (but technical) skills acquired from the pool of expertise which was available to the host group. Key examples of such additional competency acquired during the Fellowship period include quantum chemical techniques for modelling ground state geometric/electronic structure and X-ray crystallography (a very important tool for a synthetic organometallic chemist), both crystal measurement and solving the data using Crystal software. These techniques not only form a vital part of an integrated synthetic/computational approach which is typically found in most high-ranking synthetic research groups, but are also becoming widely proliferated in laboratories at a more general level. As such, key tools which were missing from my chemical toolbox were assimilated as part of this Fellowship. A second very powerful methodology, albeit less widely used currently, is in situ mass spectrometry for monitoring air-sensitive mixtures during catalytic runs; this too were also added to my list of highly applicable scientific skills during my time in Oxford.

In addition to the technical/scientific training directly related to the research proposal, with the support of the department infrastructure, this Fellowship allowed additional training for me to add complementary competencies to my career and reinforced my professional maturity and independence. This was achieved as detailed below. As preparation for an independent research career, I was involved in a series of additional activities:

(i) Complementing my own research project, I supervised two Masters level student thesis. This supervision strengthened my ability to define novel avenues of research chemistry and also assisted undergraduate and doctoral students who were facing difficulties with their research projects. In addition,

it helped me to identify breakthrough results for further development. This particular aspect of the training regimen provided key leadership/ people management skills for my independent career, as well as helped me to develop and refine the time management skills which are of course crucial to a academia career pathway.

(ii) I presented my work regularly at research group meetings, thereby improved my communication skills, and in particular my English language oral skills. As an extension of this training commitment, I was also given the opportunity to attend international meetings and present posters communications, thereby further honed my competencies in this key aspect of modern-day research. Moreover, this type of activity allowed me to meet well-established and internationally leading experts in Main Group Chemistry and facilitated networking activities. Attendance at meetings and conferences allowed the opportunity to meet not only academics but also industrialists in relevant fields.

(iii) I was involved in some of the management aspects of the group, assuming responsibility for some of the logistic aspects of running a research group within an academic institution (budget, safety, solvents, equipment, safe disposal etc.). These project/laboratory management skills are crucial to the smooth running of a research group (typically consisting of a diverse cross-section of research workers), and the logistical/people management skills so assimilated will be key in future deployment. Overall supervision in this aspect of the training was closely carried out by Prof. Aldridge.

(iv) I was also encouraged strongly to write my own publications, as this activity helped me to develop my writing/critical analysis skills, which are crucial to this absolutely key facet of scientific endeavor. As my supervisor, Prof Aldridge corrected the manuscripts derived from my research and submitted to the editor. However, the allowance of increasing freedom in the presentation/interpretation of data for publication as the Fellowship progressed stimulated competency in this vital skill. Moreover, given that the vast majority of widely read journal articles in chemistry are written in English, this one and half-year Fellowship period in Oxford offered a prime opportunity for me to develop my written English in an environment in which high quality publication output is paramount.

Thus, the facilities and expertise available in the host group and institution offered a unique opportunity for me to gain advancement in a range of areas – not only in project specific skills, but also in wider time/project management, supervision and creative aspects of academic life.

The facilities and expertise available in the host group and institution offered a unique opportunity for me to gain advancement in a number of areas – not only in project-specific chemical diversification and in the assimilation of more broadly applicable scientific techniques, but also in wider time/project management, supervision and creative aspects of academic life. The opportunities to develop my own ideas in a supportive yet constructively critical environment, to supervise more junior research workers (masters and graduate students), to present results orally to a wide audience of peers (and more senior colleagues), to

network with scientists engaged in an extremely broad range of research endeavors, to gain experience in writing papers and grant applications, and to manage/prioritize time gave invaluable experiences which translated by me into useful expertise relevant in obtaining a permanent academic position. A crucial aspect of this professional development was the exploitation of an environment in which I was able to devise, develop and assess my own research ideas. Thus, although at the outset of the project the precise details of target systems were informed more by the background experience of the host group, as the two-year period progressed every opportunity was given to me to develop my intellectual input to the project (both in the short-, medium- and longer-term). The competency so developed helped me to stand in good stead in the supervision of my own research co-workers.

The mobility facilitated by the award of a Fellowship to me not only brought with it the benefits of two-way knowledge transfer, but also the potential for significant fundamental advances in key areas of scientific endeavor set out by the European Commission. Catalysis – the ultimate goal of the project carried out – has broad ranging benefits to a number of EU priority areas, ranging from energy and healthcare (new routes to key inorganic/organic functionalities) to industrial technologies and environment (e.g. ‘greener’ atom efficient protocols carried out under milder conditions). From a knowledge transfer perspective, the two-way flow of expertise led me to broaden my chemical knowledge/skills base by assimilating from the host group knowledge of Main Group reagents/systems, and their application in bond activation and catalysis (thereby complementing my previous experience in the markedly different chemistry of the late transition elements). Moreover, members of the host group assimilated best practice in homogenous catalysis (in particular in the analysis of complex reaction mixtures by chromatography, Multi-nuclear NMR techniques, GC-mass, in situ ESI-mass spectrometry with glove box interface etc.) complemented existing expertise in fundamental structure/bonding and stoichiometric reactivity.

Both the Fellow and host brought complementary skill sets, and as such, the team was significantly greater than the sum of the parts. The mobility facilitated by this Fellowship therefore allowed chemistry to be explored which *simply could not be accomplished by either party in isolation*. While a number of the aspects of the proposed work are fundamental in their nature, representing the underpinning ground work for a range of future catalytic systems, the focus of several of the target systems as outlined in the main S&T results section is specifically aimed at exploring the viability and scope of redox-based bond modifying catalysis by Main Group metal. The vast majority of current industrial catalysts use expensive late Transition Metals (e.g. Rh, Pd, Pt); issues relating to the sustainable availability/cost of such elements and the incorporation of toxic heavy metals into products, mean that the search for alternative catalytic platforms is at the cutting edge scientifically and economically. Main group metals, by contrast, are inexpensive, abundant, and in the cases of the lighter elements (such as the germanium compounds ultimately utilized here) less of an issue with regard to toxicity. Therefore, our aim of establishing the

fundamental ground rules for catalyst design in what is an entirely new area of endeavor during the lifetime of the project. Finally, the focus on Main Group systems from bond activation and catalysis perspective is also very timely; not only do these systems may offer an alternative new perspective to the existing expensive transition metal catalysts, but they also offer an important area of research about the activation of polar/non-polar bond under mild condition. Thus a full understanding of the fundamental patterns of reactivity of these systems has significantly broader scope.

The Department of Chemistry in Oxford also has an outstanding track record in terms of the attainment by its junior research workers of permanent jobs in academia and in the chemical and related industries. Thus, the contacts which I have made, not only within the host group, but also at a broader level throughout the Department of Chemistry will offer exceptional possibilities for inter-disciplinary collaboration in the longer term. I also became a member of the graduate common room at The Queen's College, as through this association met academics from across an even broader range of expertise. Here too, the potential for lasting cooperation is borne out by the track record of previous post-doctoral researchers occupying similar positions.

With a broader geographic profile in mind, my work has given rise to four publications to date, including papers in the top-ranking chemistry journals *Journal of the American Chemical Society* (three) and *Chemistry – European Journal* (one). One further paper is under consideration currently (with *Journal of the American Chemical Society*) and a few more will be submitted in the coming six-month period. In addition, Dr Kolychev was afforded the opportunity to present his work at a number of national and international meetings, including conferences organized by the Royal Society of Chemistry (2016 RSC Coordination and Organometallic Chemistry Discussion Group Meeting, presented poster), IMEBORON 2014 meeting and the 14th International Symposium on Inorganic Ring Systems (IRIS) in Regensburg, Germany (July 2015; presented poster).

Although the research carried out is primarily fundamental in nature and mainly be of benefit to academic researchers in the short term, if any industrial collaborator is interested the University's technology transfer companies Isis Innovation (www.isis-innovation.com) will be involved to provide advice on identifying relevant industrial collaborators, exploitation of intellectual property towards wealth creation, patenting and protection of ideas, technical vetting *etc.*